his interest in the work, and also to the University of Pennsylvania for the laboratory facilities extended.

Summary

The variation of the classical dissociation constant of acetic acid with changing molecular acetic acid concentration in solutions 0.1 molar in sodium acetate and 0.9 molar in potassium or sodium chloride has been determined using the quinhydrone electrode. The stability of acetic acid–acetate buffers has been investigated.

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[CONTRIBUTION FROM THE PHYSICAL CHEMISTRY LABORATORY OF THE STATE UNIVERSITY OF IOWA]

The Vapor Pressures and Activity Coefficients of Aqueous Solutions of Perchloric Acid at 25°[1]

BY J. N. PEARCE AND A. F. NELSON

In a recent paper Pearce and Nelson[2] have reported upon the vapor pressures and activity coefficients of aqueous solutions of several alkali salts. The present paper deals with the results of a similar study of aqueous solutions of perchloric acid and these will be presented briefly. The acid is non-volatile and hence its solutions should be readily amenable to thermodynamic treatment from vapor pressure data.

The apparatus and technique, the accuracy attained and the methods of calculation are fully described in the previous paper. It may suffice to state that the vapor pressure of the solvent is calculated by means of the simple relation

$$p_1 = \frac{n_1}{n_1 + n_2} P$$

Here n_1 is the number of moles of water vapor collected in the phosphorus pentoxide absorber, while n_2 is the total number of moles of hydrogen and oxygen electrolytically generated and calculated from the amount of silver deposited in a silver coulometer. P is the corrected barometric pressure.

Chemically pure perchloric acid was further purified according to the method recommended by Willard.[3] It was twice redistilled at 162–163° under a pressure of 200 mm. Mother solutions were prepared from the concentrated acid. The exact concentrations of these were determined on a weight-concentration basis by titration with a solution of sodium hydroxide which had been standardized previously against a Bureau of Standards

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(1) A brief summary of a thesis presented by Arthus F. Nelson to the Graduate College of the State University of Iowa in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

(2) Pearce and Nelson, THIS JOURNAL, **54**, 3544 (1932).

(3) Willard, *ibid.*, **34**, 1480 (1912).

sample of acid potassium phthalate. All solutions were prepared in conductivity water and on a weight molal basis.

The essential data are collected in Table I. Here *m* is the molality, *d* is the density referred to water at 4°, and *p* is the mean of from three to seven closely agreeing independently determined vapor pressures. In no case does the average deviation from the mean exceed 0.002 mm.

TABLE I

ESSENTIAL EXPERIMENTAL DATA FOR AQUEOUS SOLUTIONS OF PERCHLORIC ACID AT 25°

m	d	P, mm.	$(p_0 - p)/p_0$	a_1
0.00000	0.997071	23.752	.....	1.0000
.10016	1.00263	23.672	0.003368	0.9967
.20064	1.00834	23.593	.006694	.9933
.40257	1.01918	23.429	.013599	.9864
.60655	1.02998	23.254	.020967	.9790
.81037	1.04087	23.067	.028839	.9712
1.01589	1.05135	22.870	.037134	.9629
2.0661	1.10322	21.693	.086687	.9133
3.1512	1.15220	20.192	.149882	.8501
4.2734	1.19970	18.387	.225875	.7742
5.4347	1.24543	16.308	.313405	.6866
6.6372	1.29023	13.935	.413312	.5867
7.8719	1.33273	11.490	.516251	.4838
9.1723	1.37386	9.016	.620410	.3797
10.5132	1.41380	6.838	.712108	.2879
11.9050	1.45283	4.982	.790249	.2067

The activity of the solvent at the various concentrations was calculated directly from the fractional lowering of the vapor pressure by means of the familiar relation proposed by Lewis and Randall,[4]

$$\ln a_1 = -\frac{p_0 - p}{p_0} - \frac{1}{2}\left(\frac{p_0 - p}{p_0}\right)^2 - \frac{1}{3}\left(\frac{p_0 - p}{p_0}\right)^3 - \dots$$

Only the first term is necessary in the most dilute solutions. With increase in concentration further terms in the series were added until the effect of an added term became negligible.

The fractional lowering of the vapor pressure produced by the perchloric acid is shown graphically in Fig. 1. For comparison we have plotted also the fractional lowering curves for some of the typical alkali halides presented in the previous paper. The $2n_2/(n_1 + 2n_2)$–molality curve represents the theoretical fractional lowering of the vapor pressure of the solvent by a completely dissociated binary electrolyte whose ions form ideal solutions. The relative positions of these curves have already been discussed[2] from the standpoint of the attraction of the water dipoles by the electrically charged ions.

However, the relations previously discussed refer rather specifically to the hydration of the cations. It is evident from Fig. 1 that solutions of

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(4) Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., 1925, p. 274.

perchloric acid are even more abnormal than those of the highly hydrated lithium chloride. Apart from the fact that the proton combines with one molecule of water to form the hydronium ion, H_3O^+, we know nothing very definite regarding the total hydration of the hydrogen ion. According to Washburn and Millard,[5] the hydration values of the hydrogen and alkali ions, N_w, are the values given in the following table, if we assign to the chloride ion the hydration values (1) zero and (2) four molecules

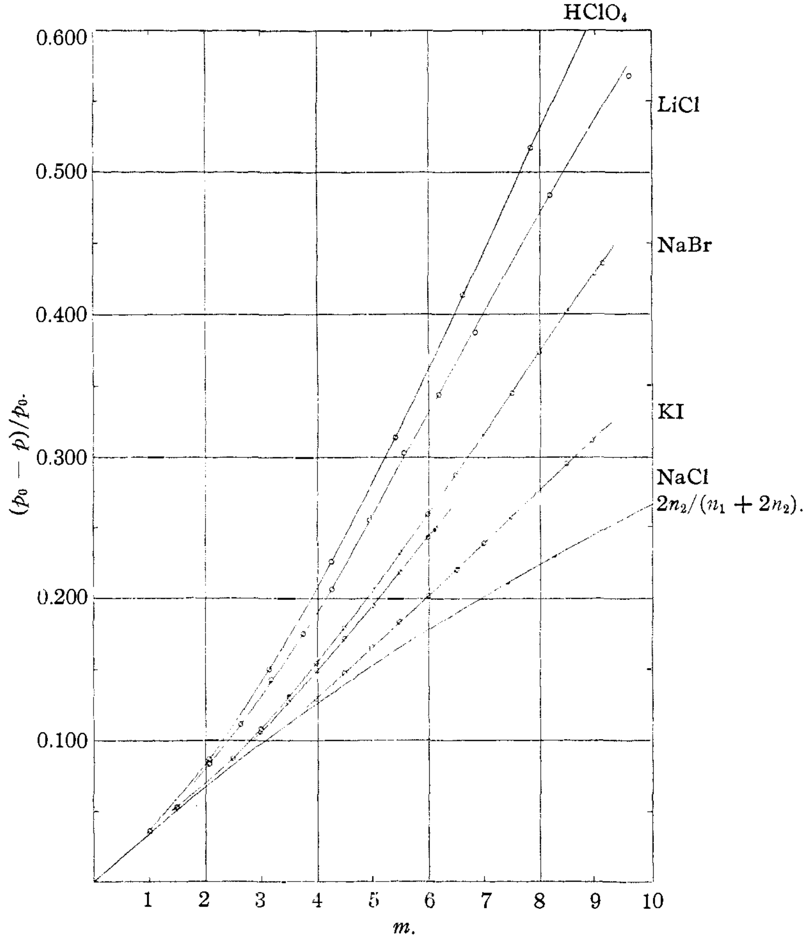

Fig. 1.

$N_w^{Cl^-}$	$N_w^{H^+}$	$N_w^{Cs^+}$	$N_w^{K^+}$	$N_w^{Na^+}$	$N_w^{Li^+}$
0	0.3	0.7	1.3	2.0	4.7
4	1.0	4.7	5.4	8.4	14.0

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(5) Washburn and Millard, THIS JOURNAL, **37**, 694 (1915).

According to these data, the hydration of the hydrogen ion is slight. For the alkali ions the order of hydration is just the reverse of the ionic volumes. On the other hand, Bjerrum[6] calculates the total hydration of the ions in a 4 *n* solution of hydrochloric acid to be nine molecules of water and two of these are held by the chloride ion.

Little is known also of the capacity of the anions to attract water dipoles. In a study of the concentration changes which occur in the presence of an inert substance during electrolysis, Nernst, Garrard and Oppermann[7] have calculated that the sulfate, chloride, bromide and nitrate ions drag with them 9, 5, 4 and 2.5 molecules of water, respectively. From the similarity and the complexity of the two ions we might infer that the hydration of the perchlorate ion should approximate that of the sulfate ion.

Jones and his co-workers[8] have found that for equivalent concentrations those salts which are most highly hydrated in the solid state are also the very salts which produce the most abnormal lowering of the freezing point of the solvent. They should, and do, produce the most abnormal lowering of the vapor pressure, and also the greatest relative lowering. Sulfuric acid produces abnormally large freezing point depressions, and definite hydrates have been found.

Sidgwick and Ewbank[9] have found that acids, bases and salts can be divided sharply into two classes: those which form solid hydrates and those which do not. The former invariably give a greater depression of the freezing point than do the latter.

Hydrates of perchloric acid have been obtained in the solid state,[10] namely, $HClO_4 \cdot 2H_2O$, $HClO_4 \cdot 2.5H_2O$, $HClO_4 \cdot 3H_2O\text{-}\alpha$, $HClO_4 \cdot 3H_2O\text{-}\beta$ and $HClO_4 \cdot 3.5H_2O$. The hydration of the ions, due to the attraction of the water dipoles by the ions, is undoubtedly somewhat greater than in the solid crystalline state. Because of the possible great tendency of both ions of perchloric acid to form hydrates in solution, by ionic attraction, we should expect the fractional lowering of the vapor pressure by perchloric acid to be greater at all concentrations than that produced by the most highly hydrated of the alkali halides. The results obtained are in harmony with the expectations.

The activity coefficients of the ions of perchloric acid were calculated with the aid of the relation[11]

$$\ln y = -\frac{h}{2.303} - \frac{2}{2.303}\int_0^{m^{1/2}} \frac{h}{m^{1/2}}\, dm^{1/2}$$

where $h = 1 + 55.51 \ln a_1/\nu m$, and $\nu = 2$. The values of h and $h/m^{1/2}$ were calculated for each concentration and the values of $h/m^{1/2}$ were then

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(6) Bjerrum, *Z. anorg. allgem. Chem.*, **109**, 275 (1919).

(7) Nernst, Garrard and Oppermann, Göttingen Nachr., 1900, p. 86.

(8) For references, see Jones and Pearce, *Am. Chem. J.*, **38**, 688 (1907).

(9) Sidgwick and Ewbank, *J. Chem. Soc.*, **125**, 2273 (1924).

(10) Van Wyk, *Z. anorg. allgem. Chem.*, **48**, 1 (1906).

(11) Randall and White, THIS JOURNAL, **48**, 2514 (1926).

plotted against the square root of the molality. Practically every one of the points fall on a perfectly smooth curve. The curve was extended to meet the ordinate at 0.394.[12] The value of the integral, which is the area under the curve from zero concentration to any desired concentration, *m*, was carefully determined by means of a polar planimeter.

A comparison of the activity of water and of the activity coefficients of the ions in perchloric and hydrochloric acid solutions should be interesting. Randall and Young[13] have calculated the activity coefficients of the ions of hydrochloric acid from freezing point, vapor pressure and electromotive force for solutions ranging from 0.001 to 16 *m*. By making the proper substitutions in the thermodynamic equation

$$d \ln a_1 = -(N_2/N_1)\,\mathrm{d} \ln a_2,$$

they finally obtain the relation

$$\ln a_1 = -\frac{2m}{55.51 \times 2.303} - \frac{2}{2.303}\int_0^m m \,\mathrm{d} \ln y$$

Thus, they were able to calculate the activity of the water in the various solutions directly from the activity coefficients of the ions. The activity coefficients of the water and the activity coefficients of the ions in solutions of both acids are collected in Table II.

It is to be noted that the activity of the water in corresponding solutions of the two acids is the same up to 2 *m*. With increase in acid concentration the activity of the water diminishes more rapidly in the perchloric acid solutions. The activity coefficients of the ions of both acids pass through a minimum value at about 0.4 *m*. Above a concentration of about 2 *m* the activity of the ions of perchloric acid increases much more rapidly and attains exceedingly high values in the highest concentrations. The lower values of the activity coefficients at the minimum and the more rapid increase at the higher concentrations in the case of the perchloric acid solutions are exactly what might be expected from the relative hydrating powers of the ions of the two acids.

The free energy change involved in the transfer of one mole of water from the pure solvent to a solution of molality *m* was calculated by means of the relation $-\Delta\bar{F}_1 = RT \ln 1/a_1$. The change in free energy accompanying the transfer of one mole of acid from any concentration, *m*, to one exactly 0.1 *m* is given by $-\Delta\bar{F}_2^{0.1} = RT \ln a_{\mathrm{m}}/a_{0.1}$. The values thus calculated are to be found in the last two columns of Table II.

Having the densities of the solutions it is a simple matter to calculate the volumes of the solutions as a function of the molalities

$$V = \alpha + \beta m + \gamma m^2$$

The differentiation of this equation with respect to *m* gives immediately an expression for the partial molal volume, $\bar{v}_2$, of the acid at the concentration

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[12] Randall, THIS JOURNAL, **48**, 2512 (1926).

[13] Randall and Young, *ibid.*, **50**, 989 (1928).

m. That is, $\bar{v}_2 = \beta + 2\gamma m$. The constants α, β and γ were evaluated by the method of least squares. The equations finally obtained were

$$V = 1003.0121 + 44.6726m + 0.1660m^2 \quad \text{and} \quad \bar{v}_2 = 44.6726 + 0.3320m$$

TABLE II

THE ACTIVITY OF THE SOLVENT AND THE ACTIVITY COEFFICIENTS OF THE IONS IN AQUEOUS SOLUTIONS OF PERCHLORIC AND HYDROCHLORIC ACIDS, AND THE CHANGE IN FREE ENERGY ACCOMPANYING THE TRANSFER OF SOLVENT AND SOLUTE IN PERCHLORIC ACID SOLUTIONS AT 25°

m	a_1 ($HClO_4$)	a_1 (HCl)	γ ($HClO_4$)	γ (HCl)	$-\Delta\bar{F}_1$ cal.	$-\Delta\bar{F}_2^{0.1}$ cal.
0.0	1.0000	1.0000	1.000	1.000	....	....
.1	0.9967	0.9966	0.771	0.796	1.99	0
.2	.9933	.9932	.731	.766	3.99	759
.4	.9863	.9862	.709	.754	8.18	1544
.6	.9790	.9789	.714	.763	12.59	2034
.8	.9717	.9712	.734	.783	17.02	2408
1.0	.9634	.9632	.803	.810	22.10	2779
2.0	.9161	.9175	1.295	1.018	51.96	4167
3.0	.8597	.8645	2.076	1.320	89.63	5208
4.0	.7940	.8040	3.287	1.762	136.77	6094
5.0	.7206	.7389	5.345	2.375	194.3	6935
6.0	.6407	.6710	9.100	3.220	263.9	7782
7.0	.5560	.6027	16.389	4.368	348.0	8663
8.0	.4722	.5361	29.641	5.957	444.9	9523
9.0	.3923	.4720	54.592	7.944	554.8	10387
10.0	.3205	.4146	146.66	10.446	675.1	11684
11.0	.2578	....	275.88	....	803.7	12547
12.0	.2047	.3162	533.55	17.25	940.5	12988

TABLE III

THE PARTIAL MOLAL VOLUMES OF WATER AND PERCHLORIC ACID AT 25°

m	$\bar{V}_2$	$\bar{V}_1$	m	$\bar{V}_2$	$\bar{V}_1$
0.0	44.673	18.068	4.0	43.345	18.117
.1	44.639	18.069	5.0	43.013	18.144
.2	44.606	18.069	6.0	42.681	18.177
.4	44.540	18.070	7.0	42.349	18.215
.6	44.473	18.070	8.0	42.017	18.260
.8	44.407	18.071	9.0	41.685	18.311
1.0	44.341	18.072	10.0	41.333	18.368
2.0	44.009	18.081	11.0	41.021	18.431
3.0	43.677	18.087	12.0	40.639	18.500

It is a simple matter now to calculate the partial molal volume, $\bar{v}_1$, of the solvent at the various concentrations by the relation

$$V = n_1\bar{v}_1 + n_2\bar{v}_2, \text{ or } \bar{v}_1 = (V - n_2\bar{v}_2)/55.51$$

The values of the partial molal volumes of the acid and water are given in Table III. It will be observed that the partial molal volume of the acid diminishes with increase in concentration, whereas that of the water increases slightly.

Summary

1. The vapor pressures of aqueous solutions of perchloric acid have been measured at 25° for concentrations ranging from 0.1 *m* to 12 *m*.

2. The activity of the water and the activity coefficients of the ions have been calculated and compared with the corresponding values for hydrochloric acid at the same concentrations and at the same temperature.

3. The free energy of transfer of both the solvent and the solute, and the partial molal volumes of both components have been calculated for each concentration.

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE]

Activity Coefficients of Salts in Anhydrous Acetic Acid Solutions from Solubility Measurements

BY A. W. SCHOLL, A. WITT HUTCHISON AND G. C. CHANDLEE

In a recent paper by Seward and Hamblet[1] activity coefficients of salts in acetic acid solutions, determined from solubility measurements, have been reported.

In the work described by the present writers similar investigations, which were in progress at the time the above results were published, have been extended to include unsymmetric valence type salts. Studies have been made on the solubility relations of potassium perchlorate in anhydrous acetic acid in the presence of sodium bromide, lithium chloride and magnesium chloride, and of barium chloride in the presence of sodium bromide. Data on the solubility of potassium perchlorate in the presence of sodium bromide were reported by Seward and Hamblet.[1] Our data are presented to show the correlation obtained.

The present data have been treated from the standpoint of the original Debye and Hückel theory[2] and according to the extended equations of Gronwall, La Mer and Sandved,[3] and of La Mer, Gronwall and Greiff.[4]

In the case of symmetrical solutes Gronwall, La Mer and Sandved[5] give a complete analytical solution of the Poisson–Boltzmann equation and the numerical tables for computations through a fifth approximation. For acetic acid solutions at 25° Seward and Hamblet[6] have evaluated the numerical constants in equation (2) of their paper. In this discussion this

(1) Seward and Hamblet, THIS JOURNAL, **54**, 554 (1932).

(2) Debye and Hückel, *Physik. Z.*, **24**, 185 (1923).

(3) Gronwall, La Mer and Sandved, *ibid.*, **29**, 358 (1928).

(4) La Mer, Gronwall and Greiff, *J. Phys. Chem.*, **35**, 2295 (1931).

(5) Gronwall, La Mer and Sandved, *Physik. Z.*, **29**, 358 (1928).

(6) Seward and Hamblet, THIS JOURNAL, **54**, 554 (1932).